

# Excitation Energies of Benzene from Kohn–Sham Theory

NICHOLAS C. HANDY, DAVID J. TOZER\*

*Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, UK*

*Received 13 July 1998; accepted 20 July 1998*

**ABSTRACT:** Singlet and triplet vertical excitation energies are determined for benzene using time-dependent Kohn–Sham density functional theory. The potential of the HCTH continuum functional is explicitly corrected, using a recently developed procedure, to impose the appropriate  $-1/r + C$  asymptotic behavior. The 48 valence ( $\pi \rightarrow \pi^*$ ) and Rydberg ( $\pi \rightarrow n = 3$ ) excitation energies computed using this corrected potential have a mean absolute error of 0.12 eV. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 106–113, 1999

**Keywords:** benzene; excited states; density functional theory

## Introduction

Kohn–Sham density functional theory (DFT) is now widely used for the calculation of ground-state properties of molecules. Both local GGA functionals (e.g., BLYP<sup>1</sup>, HCTH<sup>2</sup>) and hybrid functionals (e.g., B3LYP<sup>3</sup>) are in common use. The most successful functionals contain a set of parameters whose values have been determined in such a way that the functional gives predictions that are in best agreement with “experimental” data (e.g., energies, structures) for a chosen set of molecules.

However, much of modern chemistry involves linear response molecular properties, which arise from the response of a molecule to an external electromagnetic field. In this study we concentrate

on single-photon vertical excitation energies, which are determined in DFT through the poles of the frequency-dependent polarizability. If electric current dependence is ignored, then (by now) standard time-dependent DFT theory<sup>4–8</sup> leads to the following equation for the determination of the excitation energies,  $\omega$ , when GGA functionals are used:

$$(H_2^{\frac{1}{2}} H_1 H_2^{\frac{1}{2}} - \omega^2 I) c = 0 \quad (1)$$

where  $H_1$  is the so-called electric Hessian, given in a spin–orbital notation by:

$$(H_1)_{ai,bj} = (\epsilon_a - \epsilon_i) \delta_{ai,bj} + 2(ai|bj) + \left( ai \left| \frac{\delta v_{xc}}{\delta \rho} \right| \delta \rho(bj) \right) \quad (2)$$

Thus, orbital energy differences, two-electron integrals of the  $(x0|x0)$  variety, and one-electron integrals involving first derivatives of the exchange–

Correspondence to: N. Handy

\*Present address: Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK

correlation potential are involved. The magnetic Hessian,  $H_2$ , is positive definite diagonal, given by:

$$(H_2)_{ai,bj} = (\epsilon_a - \epsilon_i)\delta_{ai,bj} \quad (3)$$

It has been amply demonstrated, for example, by Casida et al.<sup>5</sup> and Bauernschmitt and Ahlrichs,<sup>7,9</sup> that valence excitation energies are calculated to an accuracy of  $\sim 0.3$  eV, a great improvement over the corresponding time-dependent Hartree-Fock (or RPA) predictions, and also a great improvement over single configuration interaction (SCI) predictions. However, it has been also recognized that a straightforward implementation with GGA functionals gives an extremely poor description of excitations to Rydberg states. Casida et al.<sup>5</sup> were the first to understand that this was not due to an absence of electric current dependence in the functional, but rather was due to an incorrect asymptotic exchange-correlation potential.

We have recently presented a new technique<sup>10</sup> that corrects this deficiency in the asymptotic potentials of GGA functionals. Excitation energies of several small molecules, determined using the corrected potential, are accurate for both valence and Rydberg excitations. The aim of this study is to apply this new approach to the chemically important molecule, benzene.

We observe that Grimme<sup>11</sup> has also presented accurate vertical excitation energies using a parameterized single-excitation configuration interaction approach. He uses Kohn-Sham eigenvalues, suitably scaled Coulomb contributions, and a parameterized exchange correction to the matrix elements. It is encouraging that such an approach is capable of giving good results, and we suggest that the theory in the next section may provide partial understanding of why it is successful.

## Asymptotically Corrected Exchange-Correlation Potentials

In this section we outline our new procedure for determining excitation energies using an asymptotically corrected exchange-correlation potential. Full details may be found in ref. 10.

The Kohn-Sham equation, for a GGA functional,  $E_{xc}[\rho]$ , is:

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_j(\mathbf{r}) + v_{xc}(\mathbf{r}) - \epsilon_p\right)\phi_p(\mathbf{r}) = 0 \quad (4)$$

involving the external potential,  $v_{ext}(\mathbf{r})$ , the Coulomb potential,  $v_j(\mathbf{r})$ , and the exchange-correlation potential,  $v_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$ . It is by now established that, in the energetically important regions, the form of  $v_{xc}(\mathbf{r})$  for different GGAs is similar (as is evident from their similar homo eigenvalues), and also the form of the occupied molecular orbitals is similar. However, there are substantial inadequacies in the asymptotic region. As  $r \rightarrow \infty$ , the Kohn-Sham equation for the homo orbital yields:

$$-I + 0 + 0 + v_{xc}(\infty) - \epsilon_{homo} = 0 \quad (5)$$

or:

$$v_{xc}(\infty) = I + \epsilon_{homo} \quad (6)$$

where  $I$  is the ionization potential. Because it is now well established, both by calculation and theory,<sup>12,13</sup> that for GGA functionals,  $\epsilon_{homo} \sim -I/2$ , it follows that  $v_{xc}(\mathbf{r})$  must not vanish asymptotically. Furthermore, using the property that the exchange hole contains one electron, we can conclude that the form of  $v_{xc}(\mathbf{r})$  in the asymptotic region is given by:

$$v_{xc}(\mathbf{r}) \rightarrow -\frac{1}{r} + I + \epsilon_{homo} \quad (7)$$

There is no GGA in present use that obeys this condition; most, if not all, give potentials that vanish asymptotically. As a result, very few virtual orbitals are bound, and this leads to the observed deficiencies in Rydberg excitation energies computed using regular GGA functionals.

The Kohn-Sham matrix elements involve the evaluation of  $(\eta_k|v_{xc}|\eta_l)$  by quadrature. To resolve the error in the asymptotic potential of some GGA functional, we define an asymptotically corrected (AC) exchange-correlation potential, at a grid point  $\mathbf{r}$  as:

(a) If  $r_A < \alpha\sigma_A$ , for any  $A$ ,  $v_{xc}^{AC}(\mathbf{r}) = v_{xc}^{GGA}(\mathbf{r})$

(b) If  $r_A > \beta\sigma_A$ ,  $\forall A$ ,

$$v_{xc}^{AC}(\mathbf{r}) = -\frac{1}{N} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + I + \epsilon_{homo} \quad (8)$$

where  $r_A$  is the distance of  $\mathbf{r}$  from atom  $A$ ;  $\sigma_A$  is the Bragg-Slater radius of atom  $A^{14}$ ;  $\alpha, \beta$  are numerical parameters;  $N$  is the number of electrons; and  $\rho(\mathbf{r})$  is any approximate molecular den-

sity (we use the Hartree–Fock density). If, for one or more  $A$ ,  $\alpha\sigma_A < r_A < \beta\sigma_A$ , then  $v_{xc}^{AC}(\mathbf{r})$  is obtained by a linear interpolation of the formulas given in eq. (8a) and (8b). The expression in eq. (8b) exhibits the appropriate asymptotic behavior [eq. (7)].

Kohn–Sham orbitals and eigenvalues determined using this new potential can then be used in eqs. (1)–(3) to determine excitation energies [the corrected potential is not used for the term  $\delta v_{xc}/\delta\rho$  in eq. (2)]. Preliminary studies<sup>10</sup> using the recently developed HCTH functional<sup>2</sup> suggest that values of  $\alpha$  ( $= 3.5$ ) and  $\beta$  ( $= 4.7$ ) are reasonable for the determination of excitation energies and polarizabilities. We recognize that there are many varieties of this recipe, although our investigations<sup>10</sup> clearly show that the asymptotic correction is essential if Rydberg excitation energies are to be determined accurately. It should be noted that in all except the asymptotic region, the potential is the functional derivative of a GGA functional, and indeed the change to the potential has little effect (less than  $0.001 E_h$ ) on total energies, calculated by the regular GGA expression.

Before describing the calculations on benzene using the asymptotically corrected HCTH potential, we give a little more detail of the implementation. Our program is an unrestricted KS code, but, in this closed-shell case, we slightly amended the Hessian construction to give the singlet and triplet excitation energies separately (it is interesting to note that no transformed two-electron integrals are required for the triplet states), the formulas have previously been given by Bauernschmitt and Ahlrichs.<sup>7</sup> The larger calculations, which involved determining the lowest 32 eigenvalues of a matrix exceeding 3000 in dimension, were performed using our own<sup>15</sup> version of the iterative Liu–Davidson algorithm,<sup>16</sup> which we found eminently suited to this problem. The Hessian matrix was calculated once and stored on disk. The most time-consuming part of the calculation was the evaluation, by numerical quadrature, of the exchange–correlation contributions to the  $H_1$  matrix. We found that we could use a modest quadrature, approximately 4000 points surrounding each atom. However, we stress the importance in the Kohn–Sham calculations of not removing radial grid points at large distances, because, otherwise, diffuse functions become continuum-like orbitals with near-zero (instead of positive) energies. It appears that the Euler–Maclaurin radial quadrature scheme<sup>17</sup> is advantageous in this regard. For the construction of the Hessian, the radial grid can be pruned.

## Excitation Energies of Benzene

The principal excited states of benzene of interest are those that involve an excitation from the degenerate homo  $\pi$  orbitals to the degenerate lumo  $\pi^*$  valence orbitals (and also other  $\pi \rightarrow \pi^*$  valence excitations), together with excitations from the homo orbitals to the Rydberg ( $n = 3$ ) orbitals (3s, 3p, 3d). All of our calculations were performed at CC = 1.392 Å and CH = 1.086 Å.

The relevant orbitals in our study are  $a_{2u}(\pi)$ ,  $e_{1g}(\pi)$ ,  $e_{2u}(\pi^*)$ ,  $a_{1g}(3s)$ ,  $e_{1u}(3p_x, 3p_y)$ ,  $a_{2u}(3p_z)$ ,  $e_{2g}(3d_{x^2-y^2}, 3d_{xy})$ ,  $e_{1g}(3d_{zx}, 3d_{zy})$  and  $a_{1g}(3d_{z^2})$ . In each of the tables the symmetries of the possible states are given and their experimental excitation energies taken from Lorentzon et al.<sup>18</sup> Excited states of benzene have long been a challenging problem for the theoretical chemist, stretching as far back as the days of Parr–Pariser–Pople theory. Great progress has been made in quantum chemistry, because it has conclusively demonstrated that both types of states can be calculated reliably, unlike the semiempirical theories, which can only predict the valence states. In Table I we give the quantum chemistry prediction for singlet and triplet excitation energies, using the multiconfiguration plus second-order perturbation theory CASPT2,<sup>18</sup> the second-order polarization propagator approximation SOPPA,<sup>19</sup> the random-phase approximation RPA (which is time-dependent Hartree–Fock,<sup>19</sup>) and coupled cluster CC2<sup>20</sup> methodologies. For all of these studies large basis sets with additional diffuse functions were used. It is seen that the correlated methodologies give an accuracy approaching 0.1 eV, which we understand is regarded as an ultimate desirable accuracy. There are other similar studies in the literature, such as the multireference (CASSCF) perturbation theory studies of the  $\pi \rightarrow \pi^*$  spectrum by Hashimoto et al.<sup>21</sup> We shall not comment further at this stage on these *ab initio* studies, except to say that we think that the correlated methods CASPT2, SOPPA, and CC2 are incomparably expensive and complicated compared with DFT calculations! RPA is less expensive than DFT calculations (at present) because it does not involve numerical quadrature (but of course it is less accurate).

There are several practical questions to be addressed, for which we concentrated on the singlet states. First, we examined how many occupied orbitals we could treat as frozen; that is, we did

**TABLE I.**  
**Experimental Singlet and Triplet Excitation Energies (eV) of Benzene Together with *ab initio* Calculations from Literature.**

State, transition	Exp. <sup>18</sup>	CASPT2 <sup>18</sup>	SOPPA <sup>19</sup>	RPA <sup>19</sup>	CC2 <sup>20</sup>
$1^1B_{2u}(V, \pi \rightarrow \pi^*)$	4.90	4.84	4.69	5.82	5.23
$1^1B_{1u}$	6.20	6.30	6.01	5.88	6.46
$1^1E_{1u}$	6.94	7.03	6.75	7.50	7.07
$2^1E_{2g}$	7.8?	7.90	—	—	8.91
$1^1E_{1g}(R, \pi \rightarrow 3s)$	6.334	6.38	6.18	6.54	6.45
$1^1A_{2u}(R, \pi \rightarrow 3p_x, 3p_y)$	6.932	6.86	6.70	6.94	6.97
$1^1E_{2u}$	6.953	6.91	6.76	7.11	7.02
$1^1A_{1u}$	—	6.99	6.83	7.28	7.12
$2^1E_{1u}(R, \pi \rightarrow 3p\pi)$	7.41	7.16	7.03	7.16	7.32
$1^1B_{1g}(R, \pi \rightarrow 3d_{x^2-y^2}, 3d_{xy})$	7.460	7.58	7.35	7.70	7.59
$1^1B_{2g}$	7.460	7.58	7.35	7.68	7.60
$2^1E_{1g}$	7.535	7.57	7.34	7.59	7.56
$2^1A_{1g}(R, \pi \rightarrow 3d_{zx}, 3d_{zy})$	7.81?	7.74	7.56	7.77	7.81
$1^1E_{2g}$	7.81	7.77	7.55	7.80	7.80
$1^1A_{2g}$	7.81	7.81	7.59	7.85	7.83
$3^1E_{1g}(R, \pi \rightarrow 3d_{z^2})$	—	7.57	7.40	7.73	8.88
$1^3B_{2u}(V, \pi \rightarrow \pi^*)$	5.60	5.49	5.50	5.57	—
$1^3B_{1u}$	3.94	3.89	3.75	*	—
$1^3E_{1u}$	4.76	4.49	4.48	4.70	—
$1^3E_{2g}$	7.12 / 7.74	7.12	7.41	7.24	—
$1^3E_{1g}(R, \pi \rightarrow 3s)$	—	6.34	6.14	6.44	—
$1^3A_{2u}(R, \pi \rightarrow 3p_x, 3p_y)$	—	6.80	6.64	6.82	—
$1^3E_{2u}$	—	6.90	6.74	7.08	—
$1^3A_{1u}$	—	7.00	6.84	7.28	—
$2^3E_{1u}(R, \pi \rightarrow 3p\pi)$	—	6.98	6.92	7.11	—
$1^3B_{1g}(R, \pi \rightarrow 3d_{x^2-y^2}, 3d_{xy})$	—	7.53	7.35	7.69	—
$1^3B_{2g}$	—	7.53	7.33	7.65	—
$2^3E_{1g}$	—	7.57	7.32	7.51	—
$2^3E_{2g}(R, \pi \rightarrow 3d_{zx}, 3d_{yz})$	—	7.55	7.57	7.85	—
$1^3A_{1g}$	—	7.62	7.50	7.64	—
$1^3A_{2g}$	—	7.70	7.59	7.85	—
$3^3E_{1g}(R, \pi \rightarrow 3d_{z^2})$	—	7.56	7.38	7.71	—

not allow excitations from them. We found conclusively that only the six lowest (1s) orbitals could be frozen, with any further freezing affecting some of the excitation energies by more than 0.3 eV. (This is also known to those who perform *ab initio* calculations.) All calculations were therefore performed with six frozen orbitals. The dimensions of the  $H_1$  matrix were therefore  $(m - 21) \times 15 \times (m - 21) \times 15$ , where  $m$  is the size of the basis set.

Next we examined the size of the basis set. The results of our studies are given in Table II. We found the often-used 6-31 + G\* basis ( $m = 126$ ) totally inadequate. We had great difficulty identifying some of the Rydberg states and, furthermore the valence-state predictions in Table II were substantially different from the results presented in

Table III with a much larger basis. The calculations with this 6-31 + G\* basis is a good demonstration of how to get things right for the wrong reason, because it is clearly seen in Table II that the valence  $\pi \rightarrow \pi^*$  predictions are fortuitously excellent! Instead, for our investigation, we used the 6-31G\* basis ( $m = 120$ ) together with diffuse functions at the origin (this basis gave much better agreement with the final results in Table III). Following ref. 22, we used an spd set with exponent 0.01 ( $m = 130$ ), and also examined results using two such sets, with exponents (0.01, 0.04), and (0.01, 0.004) ( $m = 140$ ). An examination of these results and the individual virtual orbitals indicated that the set (0.01, 0.04) was the best “double-zeta” quality diffuse set. We then enlarged the

**TABLE II.**  
**Singlet Excitation Energies of Benzene (eV) and Our Density Functional Calculations Using HCTH Functional both with (AC) and without Asymptotic Correction.<sup>a</sup>**

State, transition	Exp.	AC 631 + G*	631G* +(0.01)	AC 631G* +(0.01)	AC 631G* +(0.01, 0.04)	AC 631G* +(0.01, 0.004)
$1^1B_{2u}(V, \pi \rightarrow \pi^*)$	4.90	5.32	5.42	5.41	5.44	5.42
$1^1B_{1u}$	6.20	6.06	6.22	6.22	6.24	6.22
$1^1E_{1u}$	6.94	6.70	7.30	7.01	7.00	7.00
$1^1E_{1g}(R, \pi \rightarrow 3s)$	6.33	6.53	5.45	6.10	6.15	6.10
$1^1A_{2u}(R, \pi \rightarrow 3p_x, 3p_y)$	6.93	7.17	5.86	6.80	6.81	6.81
$1^1E_{2u}$	6.95	7.18	5.89	6.80	6.79	6.78
$1^1A_{1u}$	—	7.16	5.86	6.83	6.81	6.81
$2^1E_{1u}(R, \pi \rightarrow 3p\pi)$	7.41	8.16	6.08	7.35	7.34	7.35
$1^1B_{1g}(R, \pi \rightarrow 3d_{x^2-y^2}, 3d_{xy})$	7.46	—	6.33	7.48	7.39	7.48
$1^1B_{2g}$	7.46	—	6.34	7.49	7.40	7.49
$2^1E_{1g}$	7.54	—	6.34	7.49	7.41	7.49
$2^1A_{1g}(R, \pi \rightarrow 3d_{zx}, 3d_{zy})$	7.81?	—	—	7.67	7.63	7.66
$1^1E_{2g}$	7.81	—	—	7.67	7.66	7.66
$1^1A_{2g}$	7.81	—	—	7.70	7.63	7.69
$3^1E_{1g}(R, \pi \rightarrow 3d_{z^2})$	—	—	—	7.52	7.38	7.51
$2^1E_{2g}(V, \pi \rightarrow \pi^*)$	7.8/9.4	8.37	—	8.54	8.52	—

<sup>a</sup> Various basis sets augmented with spd diffuse functions.

valence basis to TZ2P,<sup>23,24</sup> which together with the double-zeta diffuse set ( $m = 248$ ), formed our definitive basis set. The final matrices with this basis were  $3405 \times 3405$ .

The results of a calculation using the 6-31G\* basis and a single spd (0.01) diffuse set, but without the asymptotic correction, are given in the fourth column of Table II. It is clearly seen that the predictions for the Rydberg states are effectively meaningless. Further calculations that show the importance of the AC correction are given for other molecules in ref. 10.

The results using the 6-31G\* and TZ2P basis sets augmented with the “double-zeta” diffuse set are given in Table III for both the singlet and triplet states (48 states in all, including the spatial degeneracies, excluding the spin degeneracies). The “experimental” triplet values are taken as the CASPT2 values from ref. 18.

We now comment on some of the DFT [TZ2P + (0.01, 0.04)spd] predictions for the individual states, and we compare them with the *ab initio* predictions in Table I.

$V(\pi \rightarrow \pi^*) B_{2u}, B_{1u}, E_{1u}$ . When compared with the experimental values, the mean absolute errors for these eight states, for DFT, SOPPA, and CASPT2, are 0.18, 0.20, and 0.13 eV, respectively. RPA fails completely for the  $^3B_{1u}$  state (the excitation energy is imaginary), and its prediction for the  $^1B_{2u}$  state is in error by 0.92 eV. This set of

predictions is typical of RPA, SOPPA, and CASPT2 accuracy from many calculations in the literature, and it is becoming clear that the DFT accuracy is also typical.<sup>5,7</sup> However, we must observe that the DFT prediction for the  $^3B_{2u}$  state is very poor (too low by 0.62 eV), for which we do not have a reason. For the  $E_{1u}$  states, the DFT-predicted oscillator strength of 0.75 is close to the CASPT2 value of 0.82. We also observe that the DFT predictions for these low-lying valence states do not seem to have a systematic error pattern; from *ab initio* calculations, the  $^3B_{2u}$  state is ionic, and the  $^1B_{2u}$  state is covalent, but both have significant errors in their DFT predictions. On the other hand, the  $^1B_{1u}$  and  $^1E_{1u}$  states are ionic and the DFT errors are much smaller.

$V(\pi(a_{2u}) \rightarrow \pi^*) E_{2g}$ . The poor CC2 prediction is explained because of the importance of double excitations ( $\pi \rightarrow \pi^*$ ) in wave function calculations for the singlet state. The experimental value is uncertain, but it must be expected that the CASPT2 value for this (covalent) singlet state (7.90 eV) is close. In the light of these two comments it is encouraging that the DFT prediction (8.37 eV) is within 0.5 eV of the CASPT2 prediction (however, see later).

$R(\pi \rightarrow 3s) E_{1g}$ . The DFT prediction for the singlet state, 6.24 eV, is close to the observed value of 6.33 eV. The CASPT2 prediction is slightly better,

TABLE III.

Low-Lying  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow (n = 3)$  Singlet and Triplet Excited States of Benzene and Our Density Functional Calculations Using Asymptotically Corrected HCTH Functional with 6-31G\* and TZ2P Basis Sets, Both Augmented with Double-Zeta Diffuse spd (0.01, 0.04) Central Set.

State, transition	Exp./ CASPT2* <sup>18</sup>	6-31G*	TZ2P
$1^1B_{2u}(V, \pi \rightarrow \pi^*)$	4.90	5.44	5.28
$1^1B_{1u}$	6.20	6.24	6.02
$1^1E_{1u}$	6.94	7.00	6.94
$2^1E_{2g}$	7.8?	8.54	8.37
$1^1E_{1g}(R, \pi \rightarrow 3s)$	6.334	6.15	6.24
$1^1A_{2u}(R, \pi \rightarrow 3p_x, 3p_y)$	6.932	6.81	6.92
$1^1E_{2u}$	6.953	6.79	6.90
$1^1A_{1u}$	6.99*	6.81	6.91
$2^1E_{1u}(R, \pi \rightarrow 3p\pi)$	7.41	7.34	7.24
$1^1B_{1g}(R, \pi \rightarrow 3d_{x^2-y^2}, 3d_{xy})$	7.460	7.39	7.50
$1^1B_{2g}$	7.460	7.41	7.52
$2^1E_{1g}$	7.535	7.41	7.51
$2^1A_{1g}(R, \pi \rightarrow 3d_{zx}, 3d_{zy})$	7.81?	7.63	7.78
$1^1E_{2g}$	7.81	7.66	7.76
$1^1A_{2g}$	7.81	7.63	7.80
$3^1E_{1g}(R, \pi \rightarrow 3d_{z^2})$	7.57*	7.38	7.45
$1^3B_{2u}(V, \pi \rightarrow \pi^*)$	5.60	5.15	4.98
$1^3B_{1u}$	3.94	4.11	4.02
$1^3E_{1u}$	4.76	4.78	4.66
$1^3E_{2g}$	7.12*	7.30	7.20
$1^3E_{1g}(R, \pi \rightarrow 3s)$	6.34*	6.11	6.21
$1^3A_{2u}(R, \pi \rightarrow 3p_x, 3p_y)$	6.80*	6.72	6.85
$1^3E_{2u}$	6.90*	6.76	6.88
$1^3A_{1u}$	7.00*	6.81	6.91
$2^3E_{1u}(R, \pi \rightarrow 3p\pi)$	6.98*	7.01	7.13
$1^3B_{1g}(R, \pi \rightarrow 3d_{x^2-y^2}, 3d_{xy})$	7.53*	7.35	7.46
$1^3B_{2g}$	7.53*	7.38	7.50
$2^3E_{1g}$	7.57*	7.37	7.48
$2^3E_{2g}(R, \pi \rightarrow 3d_{zx}, 3d_{yz})$	7.55*	7.60	7.74
$1^3A_{1g}$	7.62*	7.52	7.68
$1^3A_{2g}$	7.70*	7.66	7.78
$3^3E_{1g}(R, \pi \rightarrow 3d_{z^2})$	7.56*	7.34	7.40

the SOPPA prediction is slightly worse. The RPA prediction is in error by 0.20 eV; indeed, for all the Rydberg singlet states, the DFT predictions are far superior to the RPA predictions. The predictive accuracy of both RPA and DFT is higher for the triplet states (on the assumption that the CASPT2 predictions are within 0.1 eV of the exact values).

$R(\pi \rightarrow 3p_x, 3p_y) A_{1u}, A_{2u}, E_{2u}$ . The DFT predictions for the two observed singlet states are within 0.05 eV of the observed values, and the spread of the DFT predictions (0.02 eV) for the singlet states is smaller than the CASPT2 value (0.13 eV). The predictive accuracy of DFT is superior to that of SOPPA for all these states. The DFT oscillator strength for the  $A_{2u}$  state is 0.04 (for CASPT2 it is 0.06).

$R(\pi \rightarrow 3p\pi) E_{1u}$ . The DFT prediction for the singlet state has an error of 0.17 eV, compared with the CASPT2 and SOPPA errors of 0.25 and 0.38 eV, respectively. Indeed, this state is the most difficult for CASPT2. The DFT value for the oscillator strength is 0.12, compared with the CASPT2 value of 0.06. However, the sum of the oscillator strengths for the two  $E_{1u}$  states agree (DFT: 0.87, CASPT2: 0.88); Lorentzon et al.<sup>18</sup> stated that observation suggests that the combined oscillator strength should be close to 0.8. The DFT and CASPT2 predictions for the triplet state are very close.

$R(\pi \rightarrow 3d)$ . For the singlet states for which there are observed values, the CASPT2 predictions agree within 0.12 eV, the DFT predictions are within 0.06

eV, whereas the RPA predictions are only within 0.24 eV. The CASPT2 and DFT predictions for the triplet states are within 0.20 eV of each other for all the states.

If (and this must be questioned in the light of the  $E_{1u}$ -state difficulty) we assume that the CASPT2 *ab initio* is the most accurate set available for both the triplet and the singlet states that are not observed, it is then of interest to compare the DFT and experiment/CASPT2 predictions given in Table III, for these 48 states. We find that the mean absolute difference is only 0.12 eV. For this reason we have not undertaken a quantum defect analysis because our predictions will be very close to those already presented for CASPT2.<sup>18</sup>

DFT also predicts other low-lying triplet and singlet states. In particular, the  $\sigma(e_{2g}) \rightarrow \pi^*(e_{2u})$  transition yields valence states for  $^1A_{1u}$  (7.21),  $^1A_{2u}$  (7.34),  $^1E_{2u}$  (7.32),  $^3A_{1u}$  (7.02),  $^3A_{2u}$  (7.07), and  $^3E_{2u}$  (7.05), and the  $\sigma(e_{2g}) \rightarrow 3s(a_{1g})$  transition yields Rydberg states for  $^1E_{2g}$  (8.29) and  $^3E_{2g}$  (8.21) (excitation energies in parentheses, in electron volts). There does not appear to be any comparative studies with which these values can be compared. This is surprising because our calculations suggest that there are two  $^1E_{2g}$  states that are very close, at 8.29 and 8.37 eV.

Finally, we note that predictions using the TZ2P basis are superior to those using the 6-31G\* basis. The mean absolute errors for those states for which the observed values are reliable (22 states) for TZ2P (6-31G\*) are 0.11, 0.14 eV, respectively. This result is to be expected because the parameters for the HCTH functional and  $\alpha$  and  $\beta$  [eq. (8)] were optimized for TZ2P-quality bases. (For these 22 states the mean absolute error of CASPT2 was 0.10 eV.)

## Conclusion

The purpose of this work was to demonstrate that density functional theory can be used to obtain single-photon vertical excitation energies of molecules of both valence and Rydberg character. Benzene is the classic molecule for such a study. Forty-eight triplet and singlet states are determined to a probable mean absolute accuracy of 0.12 eV. (The mean absolute error for the 12 valence states was 0.23 eV and the maximum error was 0.62 eV.) These results were obtained using a GGA functional, HCTH, which has a potential that has been suitably adjusted in the asymptotic re-

gion. The cost of the method is essentially the same as any method that involves a single excitation matrix. From these and other studies it does not appear necessary to include any electric current dependence in the functional. This may be very important, because the so-called magnetic Hessian is strictly diagonal, and therefore first-order changes in the Kohn–Sham orbitals are obtained by “uncoupled theory.” It is quite clear that it is the accuracy of the occupied and virtual orbitals and their energy that are all-important.

It is of much interest that DFT can produce this accuracy for these excited states. DFT probably has its greatest role in applications to larger molecular problems, which will always be impossible in wave function quantum chemistry. Our code for these calculations is grossly inefficient; for example, no tests for small quantities have been included in the numerical evaluation of the exchange-correlation contribution to the electric Hessian. However, the calculations in this study demonstrate that DFT is competitive with wave-function quantum chemistry for excitation energies. This will be of great importance in future studies.

## Acknowledgments

The authors are grateful for constructive comments from Prof. B. O. Roos, which have been included in this work.

## References

1. Becke, A. D. *Phys Rev A* 1988, 38, 3098; Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
2. Hamprecht, F. A.; Cohen, A.; Tozer, D. J.; Handy, N. C. *J Chem Phys* 1998, 109, 6264.
3. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J Phys Chem* 1994, 98, 11623.
4. Petersilka, M.; Gross, E. K. U. *Int J Quantum Chem Symp* 1996, 30, 181.
5. Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J Chem Phys* 1998, 108, 4439.
6. Casida, M. E. In D. P. Chong (Ed.) *Recent Advances in Density Functional Methods, Part 1*; Singapore: World Scientific, 1995; p. 155.
7. Bauernschmitt, R.; Ahlrichs, R. *Chem Phys Lett* 1996, 256, 454.
8. Colwell, S. M.; Handy, N. C.; Lee, A. M. *Phys Rev A* 1996, 53, 1316.
9. Bauernschmitt, R.; Haser, M.; Treutler, O.; Ahlrichs, R. *Chem Phys Lett* 1997, 294, 573.

10. Tozer, D. J.; Handy, N. C. *J Chem Phys* (in press).
11. Grimme, S. *Chem Phys Lett* 1996, 259, 128.
12. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys Rev Lett* 1982, 49, 1691.
13. Perdew, J. P.; Levy, M. *Phys Rev Lett* 1983, 51, 1884.
14. Slater, J. C. *J Chem Phys* 1964, 41, 3199 (but for H we use 0.35).
15. Carter, S.; Bowman, J. M.; Handy, N. C. *Theoret Chem Acc* (in press).
16. Liu, B. (a) The Simultaneous Expansion Method. *Proceedings of the Workshop on Numerical Algorithms in Chemistry: Algebraic Methods*; National Resource for Computations in Chemistry: Berkeley, CA, 1978; p. 49; (b) Davidson, E. R. *J Comput Phys* 1975, 17, 87.
17. Murray, C. W.; Handy, N. C.; Laming, G. J. *Molec Phys* 1993, 78, 997.
18. Lorentzon, J.; Malmquist, P.-A.; Fulscher, M.; Roos, B. O. *Theor Chim Acta* 1995, 91, 91.
19. Packer, M. J.; Dalskov, E. K.; Enevoldsen, T.; Jensen, H. J.; Oddershede, J. *J Chem Phys* 1996, 105, 5886.
20. Christiansen, O.; Koch, H.; Halkier, A.; Jorgensen, P.; Helgaker, T.; de Meras, A. S. *J Chem Phys* 1996, 105, 6921.
21. Hashimoto, T.; Nakano, H.; Hirao, K. *J Chem Phys* 1996, 104, 6244.
22. Christiansen, O.; Koch, H.; Jorgensen, P.; Helgaker, T. *Chem Phys Lett* 1996, 263, 530.
23. Dunning, T. H. *J Chem Phys* 1971, 55, 716.
24. Huzinaga, S. *J Chem Phys* 1965, 42, 1293.